

## Transport- and Thermo-mechanical Properties of Sr-, Mg-, Fe-, V- Co-doped Lanthanum Chromites

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Transport properties (electronic and ionic conductivity), and thermo-mechanical properties (TEC and expansion on reduction) of three co-doped lanthanum chromites  $\text{La}_{0.8}\text{Sr}_{0.2}\text{Cr}_{0.87}\text{Fe}_{0.1}\text{V}_{0.03}\text{O}_3$ ,  $\text{La}_{0.9}\text{Sr}_{0.1}\text{Cr}_{0.87}\text{Mg}_{0.1}\text{V}_{0.03}\text{O}_3$  and  $\text{La}_{0.8}\text{Sr}_{0.2}\text{Cr}_{0.97}\text{V}_{0.03}\text{O}_3$  were determined using dilatometry, high-temperature X-ray-diffraction, thermogravimetry and four point steady state and transient conductivity measurements. All measurements were conducted at a range of  $p\text{O}_2$  values. Differences in behavior are discussed in terms of simple structural models based on Shannon ionic radii.

Alkaline earth doped lanthanum chromites have been widely studied because they are thermodynamically stable at high temperature under oxidizing as well as highly reducing conditions whilst possessing high electronic conductivity (tens of S/cm in air). For these reasons they can be used as interconnect material in solid oxide fuel cell stacks (1), (2).

The acceptor doped chromites are predominantly electronic conductors, but do show some ionic conductivity as well. When used as interconnect this will result in an ionic leak current from the cathode to the anode side of the interconnect representing a parasitic consumption of fuel. Hence, the ionic conductivity is a drawback for the use as interconnect and also for the use as protective coatings on metals. In other applications, such as for use as catalyst or as SOFC anode some ionic conductivity is probably advantageous.

The acceptor doped chromites are well known to expand on reduction (3). The loss of oxygen from the material, and the associated reduction of the chromium ions, is accompanied by a volume expansion, giving rise to stresses that may in some cases be detrimental for the component (4). For the technological use of the doped chromites it is thus important to know both transport properties (ionic and electronic conductivity) as well as the thermo-mechanical properties.

The electronic conductivity and the TEC increase with increasing amounts of aliovalent doping, but so does the magnitude of the expansion on reduction. Hence, it is difficult to maximize conductivity and achieve good TEC-matching to the YSZ-electrolytes whilst minimizing the expansion on reduction. In a search for materials that meet these partly conflicting requirements a great number of co-doped lanthanum chromites have been investigated (5, 6, 7). Here, the properties of the two co-doped chromites,  $\text{La}_{0.8}\text{Sr}_{0.2}\text{Cr}_{0.88}\text{Fe}_{0.09}\text{V}_{0.03}\text{O}_3$  (LSCF) and  $\text{La}_{0.9}\text{Sr}_{0.1}\text{Cr}_{0.88}\text{Mg}_{0.09}\text{V}_{0.03}\text{O}_3$  (LSCM) are compared to the behavior of the only Sr-containing end-member of the series,  $\text{La}_{0.8}\text{Sr}_{0.2}\text{Cr}_{0.97}\text{V}_{0.03}\text{O}_3$  (LSC).

The expansion on reduction (between air and a  $p\text{O}_2$  of  $10^{-16}$  atm. (-967 mV vs. air)) determined by dilatometry was 0.18 %, 0.09 %, 0.12 % for the LSCF, LSCM and LSC, respectively. From the high temperature X-ray diffraction measurements, expansions of 0.15 % and 0.08 % were found for LSCF and LSCM, respectively, which is in good agreement with the dilatometry results. The thermal expansion coefficients of the materials (average between room temperature and 1000 °C) were 10.6, 10.0 and  $10.5 \cdot 10^{-6} \text{ K}^{-1}$  for LSCF, LSCM and LSC, respectively.

The electronic conductivities of all three materials were observed to decrease with decreasing  $p\text{O}_2$  as is typical for this type of materials. The results were analyzed using a simple point defect model (8, 9), that in the case of the iron-containing sample was generalized to take into account two redox-couples.

The oxygen diffusion constant, as determined by the conductivity relaxation method was found to increase with decreasing  $p\text{O}_2$ . For the LSC-sample, D was found to be  $1.2 \cdot 10^{-5} \text{ cm}^2/\text{s}$  at a  $p\text{O}_2$  of  $1 \cdot 10^{-16}$  atm. The surface exchange rate constant, K, determined at the same  $p\text{O}_2$  was  $2 \cdot 10^{-4} \text{ cm/s}$ . K was found to increase slightly with decreasing  $p\text{O}_2$ . For the Fe- and Mg-containing samples somewhat lower values of both K and D was found. At  $10^{-16}$  atm. D was  $5 \cdot 10^{-6} \text{ cm}^2/\text{s}$  for LSCF and ca.  $2 \cdot 10^{-6} \text{ cm}^2/\text{s}$  for LSCM, whilst K was on the order of  $5 \cdot 10^{-5}$  to  $1 \cdot 10^{-4} \text{ cm/s}$ .

The oxygen leakage fluxes through an interconnect plate of the investigated materials are calculated, as are the overall strains and stresses caused by the dimensional instability. Analytical expressions for the latter problem are presented.

The reason for the differences in behavior between the three materials is discussed in terms of a simple structural picture considering the “misfit-stresses” arising from I) the differences between measured unit-cell volumes and calculated ideal unit cell volumes assuming Shannon ionic radii and either the A-O or the B-O sub-lattice to be structurally dominating, and II) local size differences between majority and minority species.

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